

10/535,604
~~10/494,005~~

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and display fields
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NEWS 13 JUL 11 CHEMSAFE reloaded and enhanced
NEWS 14 JUL 14 FSTA enhanced with Japanese patents
NEWS 15 JUL 19 Coverage of Research Disclosure reinstated in DWPI

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MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP),
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10/494,005

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TOTAL

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SESSION

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0.21

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DICTIONARY FILE UPDATES: 25 JUL 2006 HIGHEST RN 895581-37-0

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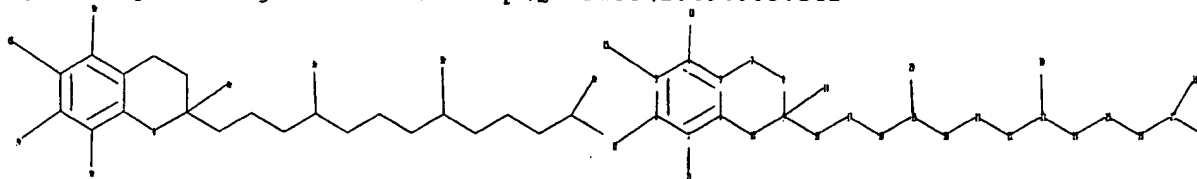
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=>

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chain nodes :

11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

ring nodes :

1 2 3 4 5 6 7 8 9 10

chain bonds :

1-13 2-12 3-15 4-11 9-14 9-16 16-17 17-18 18-19 19-20 19-29 20-21 21-22
22-23 23-24 23-30 24-25 25-26 26-27 27-28 27-31

ring bonds :

1-2 1-6 2-3 3-4 4-5 5-6 5-7 6-10 7-8 8-9 9-10

exact/norm bonds :

10/494,005

3-15

exact bonds :

1-13 2-12 4-11 5-7 6-10 7-8 8-9 9-10 9-14 9-16 16-17 17-18 18-19 19-20
19-29 20-21 21-22 22-23 23-24 23-30 24-25 25-26 26-27 27-28 27-31

normalized bonds :

1-2 1-6 2-3 3-4 4-5 5-6

isolated ring systems :

containing 1 :

Match level :

1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom
11:CLASS 12:CLASS 13:CLASS 14:CLASS 15:CLASS 16:CLASS 17:CLASS 18:CLASS
19:CLASS 20:CLASS 21:CLASS 22:CLASS 23:CLASS 24:CLASS 25:CLASS 26:CLASS
27:CLASS 28:CLASS 29:CLASS 30:CLASS 31:CLASS

L1 STRUCTURE UPLOADED

=> s l1

SAMPLE SEARCH INITIATED 09:36:47 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 153 TO ITERATE

100.0% PROCESSED 153 ITERATIONS

12 ANSWERS

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**

BATCH **COMPLETE**

PROJECTED ITERATIONS: 2318 TO 3802

PROJECTED ANSWERS: 33 TO 447

L2 12 SEA SSS SAM L1

=> s l1 ful

FULL SEARCH INITIATED 09:36:53 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 3248 TO ITERATE

100.0% PROCESSED 3248 ITERATIONS

197 ANSWERS

SEARCH TIME: 00.00.01

L3 197 SEA SSS FUL L1

=> file caplus

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

166.94

167.15

FILE 'CAPLUS' ENTERED AT 09:37:03 ON 26 JUL 2006

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10/494,005

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FILE LAST UPDATED: 25 Jul 2006 (20060725/ED)

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=> s l3 or tocopherol

17051 L3

30106 TOCOPHEROL

9187 TOCOPHEROLS

32775 TOCOPHEROL

(TOCOPHEROL OR TOCOPHEROLS)

L4 33457 L3 OR TOCOPHEROL

=> s l4 and (process or prepar? or method or syntheses? or make or made)

2274190 PROCESS

1543097 PROCESSES

3395598 PROCESS

(PROCESS OR PROCESSES)

1662507 PREPAR?

123703 PREP

2164 PREPS

125661 PREP

(PREP OR PREPS)

2018858 PREPD

17 PREPDS

2018870 PREPD

(PREPD OR PREPDS)

123870 PREPG

12 PREPGS

123881 PREPG

(PREPG OR PREPGS)

2724910 PREPN

205067 PREPNS

2879604 PREPN

(PREPN OR PREPNS)

4770926 PREPAR?

(PREPAR? OR PREP OR PREPD OR PREPG OR PREPN)

3142466 METHOD

1285786 METHODS

4066104 METHOD

(METHOD OR METHODS)

1546677 SYNTHES?

234598 MAKE

182871 MAKES

404845 MAKE

(MAKE OR MAKES)

1216756 MADE

25 MADES

1216777 MADE

(MADE OR MADES)

L5 13224 L4 AND (PROCESS OR PREPAR? OR METHOD OR SYNTHES? OR MAKE OR MADE)

10/494,005

=> s 15 and phytyltrimethylhydroquinone
2 PHYTYLTRIMETHYLHYDROQUINONE
L6 1 L5 AND PHYTYLTRIMETHYLHYDROQUINONE

=> d 16 ibib hitstr abs

L6 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2003:356435 CAPLUS
DOCUMENT NUMBER: 138:354126
TITLE: Manufacture of (all-rac)- α -tocopherol
via acid-catalyzed ring closure
INVENTOR(S): Bonrath, Werner; Burdick, David Carl; Netscher,
Thomas; Schager, Frank; Thomas, Dominik
PATENT ASSIGNEE(S): Roche Vitamins A.-G., Switz.
SOURCE: PCT Int. Appl., 20 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

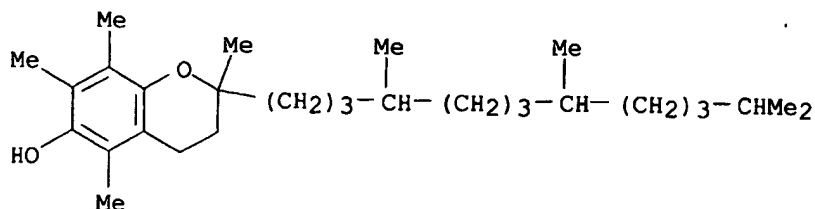
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2003037883	A1	20030508	WO 2002-EP11819	20021023
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW			
RW:	GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
EP 1446398	A1	20040818	EP 2002-785282	20021023
EP 1446398	B1	20050413		
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK			
CN 1578777	A	20050209	CN 2002-821423	20021023
JP 2005507422	T2	20050317	JP 2003-540164	20021023
AT 293108	E	20050415	AT 2002-785282	20021023
US 2005187393	A1	20050825	US 2003-494005	20021023
ES 2239260	T3	20050916	ES 2002-2785282	20021023
PRIORITY APPLN. INFO.:			EP 2001-125966	A 20011031
			WO 2002-EP11819	W 20021023

OTHER SOURCE(S): CASREACT 138:354126

IT 10191-41-0P, all-rac- α -Tocopherol
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of (all-rac)- α -tocopherol via acid-catalyzed ring closure)

RN 10191-41-0 CAPLUS

CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)- (9CI) (CA INDEX NAME)



AB A process for the manufacture of (all-rac)- α -tocopherol comprises submitting isolated, purified phytyltrimethylhydroquinone** * to acid catalysis, thereby promoting ring closure to (all-rac)- α -***tocopherol. The process can be conducted in the absence or presence of an added solvent, and when a solvent or solvent mixture is used the solvent or at least one solvent component of the solvent mixture is preferably one with a dipole moment greater than 9×10^{-30} C-m (or 2.7 D). The nature of the catalyst is immaterial, but the catalyst is preferably sulfuric acid, phosphoric acid, a polyperfluoroalkylenesulfonic acid, a 'NH-acid', a heteropoly acid, zinc chloride, boron trifluoride, aluminum trichloride, or a mixture of any of the aforementioned Broensted acids with any of the aforementioned Lewis acids. The product of the process is the most active an industrially most important member of the vitamin E group. Thus, phytyltrimethylhydroquinone in propylene carbonate and sulfuric acid in heptane were refluxed at 100°C for 1 h to give (all-rac)- α -tocopherol in 98.1% yield.

REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> s 15 and ?trimethylhydroquinone
843 ?TRIMETHYLHYDROQUINONE
L7 298 L5 AND ?TRIMETHYLHYDROQUINONE

=> s 17 and catalyst
728660 CATALYST
731617 CATALYSTS
935107 CATALYST
(CATALYST OR CATALYSTS)
L8 134 L7 AND CATALYST

=> s 18 and ring closure
489173 RING
128141 RINGS
567129 RING
(RING OR RINGS)
85587 CLOSURE
2856 CLOSURES
87270 CLOSURE
(CLOSURE OR CLOSURES)
60700 RING CLOSURE
(RING(W)CLOSURE)
L9 10 L8 AND RING CLOSURE

=> d rem 19 16
L6 IS NOT VALID HERE
For an explanation, enter "HELP DISPLAY".

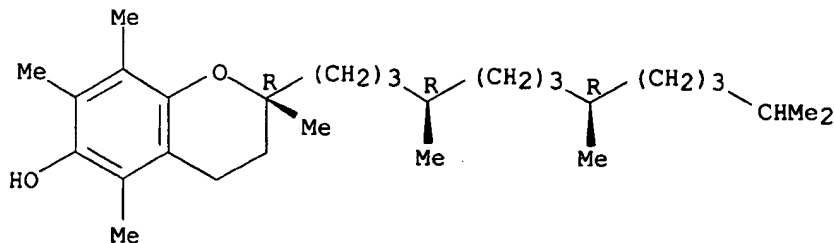
10/494,005

=> d 19 ibib hitstr abs 1-10

L9 ANSWER 1 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2005:523441 CAPLUS
DOCUMENT NUMBER: 143:60110
TITLE: Process for the manufacture of alkenylated
hydroxylated aromatic compounds, of chroman compounds
and of their acylated derivatives
INVENTOR(S): Bonrath, Werner; Foricher, Yann; Netscher, Thomas;
Wildermann, Angela
PATENT ASSIGNEE(S): DSM IP Assets B. V., Neth.
SOURCE: PCT Int. Appl., 54 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005054223	A2	20050616	WO 2004-EP13788	20041203
WO 2005054223	A3	20051027		
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
US 2005171362	A1	20050804	US 2004-5402	20041206
PRIORITY APPLN. INFO.:			EP 2003-27992	A 20031205
			EP 2004-13714	A 20040611
OTHER SOURCE(S):	CASREACT 143:60110; MARPAT 143:60110			
IT 59-02-9P, α - Tocopherol 10191-41-0P				
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)				
(preparation and acylation of; process for the manufacture of alkenylated hydroxylated aromatic compds., of chroman compds. and of their acylated derivs.)				
RN 59-02-9 CAPLUS				
CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-[(4R,8R)-4,8,12-trimethyltridecyl]-, (2R)- (9CI) (CA INDEX NAME)				

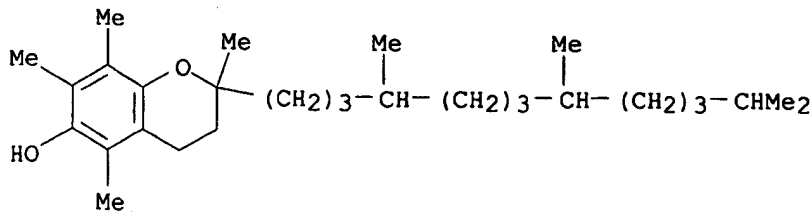
Absolute stereochemistry.



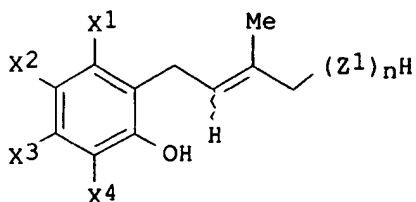
10/494,005

RN 10191-41-0 CAPLUS

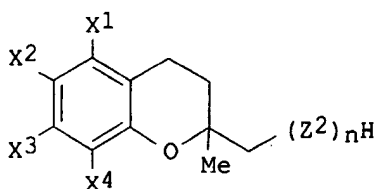
CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)- (9CI) (CA INDEX NAME)



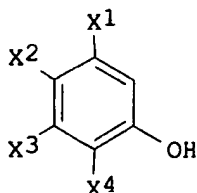
GI



I



II

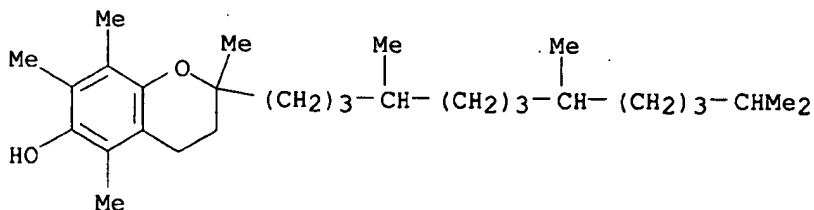


III

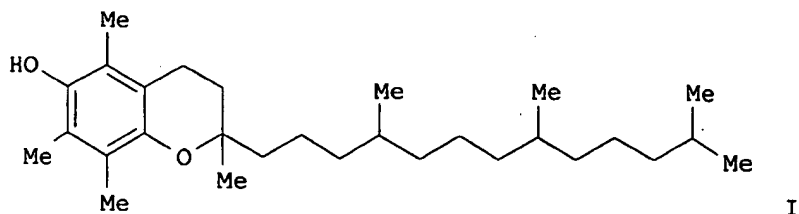
AB The present invention relates to a novel process for the manufacture of alkenylated aromatic compds., (E/Z)-I [X1, X2, X3, X4 = H, OH, linear C1-6-alkyl; Z1 = CH2CH2CMeCH2; n = 0 - 3], their ring-closure reactions to chroman derivs. II [X1, X2, X3, X4 = H, OH, linear C1-6-alkyl; Z2 = CH2CH2CMeCH2; n = 0 - 3], as well as the acylation of the latter with the aromatic moiety featuring at least one hydroxy group themselves. The present invention relates especially to a process for the manufacture of tocol, tocopherols and their alkanooates such as α -tocopherol (TCP) and alkanooates (TCPA) thereof, preferably α -tocopheryl acetate (TCPAc). The processes of the present invention are characterized in that at least one step of the processes is carried out in the presence of an indium salt as the catalyst. Thus, an object of the present invention is the use of an indium salt as the catalyst in Friedel-Crafts alkylation reactions of aromatic compds. III featuring at least one hydroxy group with R2CMe(CH:CH2)CH2(CH2CH2CHMeCH2)nH [R2 = OH, OAc, O2CPh, halogen] or (E/Z)-R2CH2CH:CMeCH2(CH2CH2CHMeCH2)nH and ring-closure

reactions of the latter to produce chroman-ring compds. in organic solvents. According to another aspect of the invention indium salts can be used as the catalyst in processes for the manufacture of tocyl alkanoates, tocopheryl alkanoates and alkanoates of aromatic compds. featuring at least one hydroxy group by reacting tocyls, tocopherol and aromatic compds. featuring at least one hydroxy group, resp., with an acylating agent. Suitable indium salts are indium(III) salts, especially indium trichloride, indium tribromide or indium triiodide, indium(III) triflate, indium(III) bis(trifluoromethanesulfonamide) and indium(III) acetate. In preferred embodiments of the invention the processes are carried out at a pressure of at least 0.96 bar, whereby the acylation can be carried out at an absolute pressure of at least 0.02 bar.

L9 ANSWER 2 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2005:374554 CAPLUS
 DOCUMENT NUMBER: 144:331565
 TITLE: Polyfluorinated strong Bronsted acids as efficient catalysts in vitamin E chemistry
 AUTHOR(S): Netscher, T.; Bonrath, W.; Haas, A.; Hoppmann, E.; Pauling, H.
 CORPORATE SOURCE: Research and Development, DSM Nutritional Products, Basel, Switz.
 SOURCE: European Symposium on Organic Chemistry, 13th, Cavtat-Dubrovnik, Croatia, Sept. 10-15, 2003 (2003), 43-45. Monduzzi Editore: Bologna, Italy.
 CODEN: 69GUWD; ISBN: 88-7587-009-8
 DOCUMENT TYPE: Conference; (computer optical disk)
 LANGUAGE: English
 IT 10191-41-0P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (polyfluorinated strong Bronsted acids as efficient catalysts in the preparation of (all-rac)- α -tocopherol via a tandem Friedel-Crafts alkylation/ring-closure reaction)
 RN 10191-41-0 CAPLUS
 CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)- (9CI) (CA INDEX NAME)



GI



AB The application of polyfluorinated NH- and CH-acidic catalysts to the synthesis of (all-rac)- α -tocopherol (I) starting from trimethylhydroquinone and isophytol is described. The scope and limitations of these highly efficient catalysts are discussed. The advantages of the new procedures are high yield and selectivity, no waste problem, and mild reaction conditions. The best results in the synthesis of (all-rac)- α -tocopherol (I) using NH-acidic imides (94% yield) and tris(perfluoroalkylsulfonyl)met hides or their salts as catalysts (up to 96% yield) were obtained in polar solvents.

REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L9 ANSWER 3 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2005:55221 CAPLUS

DOCUMENT NUMBER: 142:156178

TITLE: Manufacture of tocopherols using a bismuth catalyst

INVENTOR(S): Bonrath, Werner; Giraudi, Lisa

PATENT ASSIGNEE(S): DSM IP Assets B.V., Neth.

SOURCE: PCT Int. Appl., 23 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005005407	A1	20050120	WO 2004-EP7026	20040629
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
EP 1641772	A1	20060405	EP 2004-740420	20040629
R:	CH, LI			
PRIORITY APPLN. INFO.:			EP 2003-15368	A 20030708
			WO 2004-EP7026	W 20040629
OTHER SOURCE(S):	CASREACT 142:156178; MARPAT 142:156178			
IT 10191-41-OP,	(all-rac)- α -Tocopherol			
RL:	IMF (Industrial manufacture); SPN (Synthetic preparation); PREP			

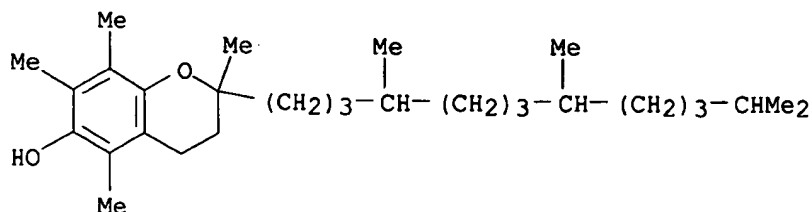
10/494,005

(Preparation)

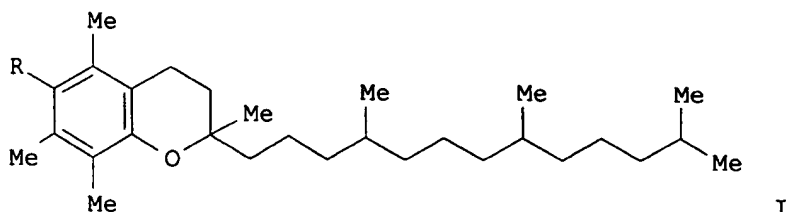
(manufacture of tocopherols via Friedel-Crafts type alkylation reactions using a bismuth catalyst)

RN 10191-41-0 CAPLUS

CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)- (9CI) (CA INDEX NAME)



GI



AB A novel process was disclosed for the manufacture of tocopherols, especially (all-rac)- α -tocopherol I (R = OH), and (all-rac)- α -tocopheryl acetate I (R = OAc) by the reaction of a hydroquinone comprising 0 to 3 Me groups, especially 2,3,5-trimethylhydroquinone, or 2,3,6-trimethylhydroquinone 1-monoacetate, resp., with isophytol, phytol or a(n) (iso)phytol derivative, most preferably with isophytol, in the presence of bismuth(III) trifluoromethanesulfonate, Bi(OSO₂CF₃)₃, as the catalyst in an organic solvent or a biphasic solvent system. A further object of the invention is the use of Bi(OSO₂CF₃)₃ as the catalyst in Friedel-Crafts type alkylation reactions and ring-closure reactions in organic solvents.

REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L9 ANSWER 4 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2004:453199 CAPLUS

DOCUMENT NUMBER: 141:7308

TITLE: Manufacture of tocopheryl acetate

INVENTOR(S): Bonrath, Werner; Dittel, Claus; Netscher, Thomas; Pabst, Thomas; Schmid, Rudolf

PATENT ASSIGNEE(S): DSM IP Assets B.V., Neth.

SOURCE: PCT Int. Appl., 26 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004046126	A1	20040603	WO 2003-EP10789	20030929
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
AU 2003271655	A1	20040615	AU 2003-271655	20030929
EP 1562929	A1	20050817	EP 2003-753473	20030929
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK				
CN 1701066	A	20051123	CN 2003-825343	20030929
JP 2006515280	T2	20060525	JP 2004-552466	20030929
US 2006094886	A1	20060504	US 2005-535604	20050519
PRIORITY APPLN. INFO.:			EP 2002-25989	A 20021121
			WO 2003-EP10789	W 20030929

OTHER SOURCE(S): CASREACT 141:7308; MARPAT 141:7308

AB A process for the manufacture of 3-phytyl-2,5,6-trimethylhydroquinone-1-acetate, and optionally tocopheryl acetate, by either C-alkylating 2,3,6-trimethylhydroquinone-1-acetate with isophytol or phytol in the presence of a sulfur(VI) containing catalyst of the formula R_1SO_2OH (R_1 = hydroxy, halogen, lower alkyl, halogenated lower alkyl or aryl) in an aprotic organic solvent, or O-alkylating 2,3,6-trimethylhydroquinone-1-acetate with a phytol halide in a polar aprotic organic solvent in the presence of a base, and subjecting the so-obtained 4-O-phytyl-2,3,6-trimethylhydroquinone-1-acetate to a rearrangement reaction, and in each case optionally submitting the so-obtained 3-phytyl-2,5,6-trimethylhydroquinone-1-acetate to a ring closure reaction to produce tocopheryl acetate. The invention also includes the novel compound 3-phytyl-2,5,6-trimethylhydroquinone-1-acetate and certain stereoisomers thereof, and also the further novel compound 4-hydroxy-2,3,6-trimethyl-5-[3-(4,8,12-trimethyltridecyl)-but-3-enyl]phenyl acetate which itself is one of several isomers of 3-phytyl-2,5,6-trimethylhydroquinone-1-acetate formed by isomerization under the influence of heating, e.g. during its distillation as part of the isolation and purification procedure following its manufacture as indicated above. (All-rac)- α - tocopherol, which may be derived from its acetate, is known to be the most active industrially important member of the vitamin E group.

L9 ANSWER 5 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2003:356435 CAPLUS

DOCUMENT NUMBER: 138:354126

TITLE: Manufacture of (all-rac)- α - tocopherol
via acid-catalyzed ring closure

INVENTOR(S): Bonrath, Werner; Burdick, David Carl; Netscher,
Thomas; Schager, Frank; Thomas, Dominik

PATENT ASSIGNEE(S): Roche Vitamins A.-G., Switz.

SOURCE: PCT Int. Appl., 20 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2003037883	A1	20030508	WO 2002-EP11819	20021023
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1446398	A1	20040818	EP 2002-785282	20021023
EP 1446398	B1	20050413		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK				
CN 1578777	A	20050209	CN 2002-821423	20021023
JP 2005507422	T2	20050317	JP 2003-540164	20021023
AT 293108	E	20050415	AT 2002-785282	20021023
US 2005187393	A1	20050825	US 2003-494005	20021023
ES 2239260	T3	20050916	ES 2002-2785282	20021023
PRIORITY APPLN. INFO.:			EP 2001-125966	A 20011031
			WO 2002-EP11819	W 20021023

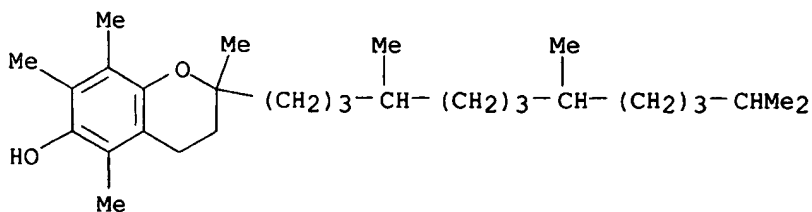
OTHER SOURCE(S): CASREACT 138:354126

IT 10191-41-0P, all-rac- α - Tocopherol

RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of (all-rac)- α - tocopherol via acid-catalyzed ring closure)

RN 10191-41-0 CAPLUS

CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)- (9CI) (CA INDEX NAME)



AB A process for the manufacture of (all-rac)- α - tocopherol comprises submitting isolated, purified phytyltrimethylhydroquinone**
* to acid catalysis, thereby promoting ***ring closure to (all-rac)- α - tocopherol. The process can be conducted in the absence or presence of an added solvent, and when a solvent or solvent mixture is used the solvent or at least one solvent component of the solvent mixture is preferably one with a dipole moment greater than 9×10^{-30} C-m (or 2.7 D). The nature of the catalyst is immaterial, but the catalyst is preferably sulfuric acid, phosphoric acid, a polyperfluoroalkylenesulfonic acid, a 'NH-acid', a heteropoly acid, zinc chloride, boron trifluoride, aluminum trichloride, or a mixture of any of the aforementioned Broensted acids with any of the

10/494,005

aforementioned Lewis acids. The product of the process is the most active an industrially most important member of the vitamin E group. Thus, phytyltrimethylhydroquinone in propylene carbonate and sulfuric acid in heptane were refluxed at 100°C for 1 h to give (all-rac)- α -tocopherol in 98.1% yield.

REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L9 ANSWER 6 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2002:239437 CAPLUS

DOCUMENT NUMBER: 137:109397

TITLE: Synthesis of (all-rac)- α -tocopherol using fluorinated NH-acidic catalysts

AUTHOR(S): Bonrath, Werner; Haas, Alois; Hoppmann, Eike; Netscher, Thomas; Pauling, Horst; Schager, Frank; Wildermann, Angela

CORPORATE SOURCE: Research and Development, Roche Vitamins Ltd, Basel, 4070, Switz.

SOURCE: Advanced Synthesis & Catalysis (2002), 344(1), 37-39
CODEN: ASCAF7; ISSN: 1615-4150

PUBLISHER: Wiley-VCH Verlag GmbH

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 137:109397

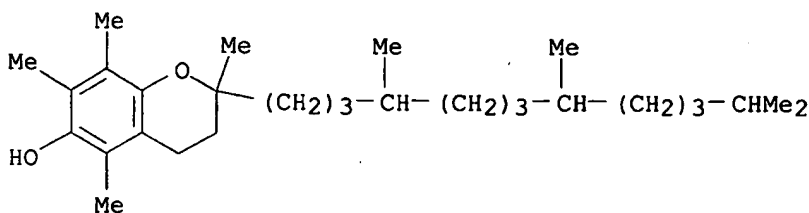
IT 10191-41-0P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

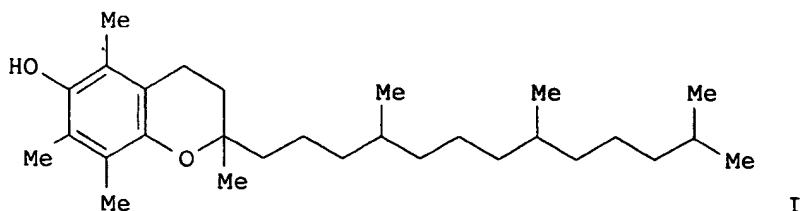
(synthesis of (all-rac)- α -tocopherol using fluorinated NH-acidic catalysts)

RN 10191-41-0 CAPLUS

CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)- (9CI) (CA INDEX NAME)



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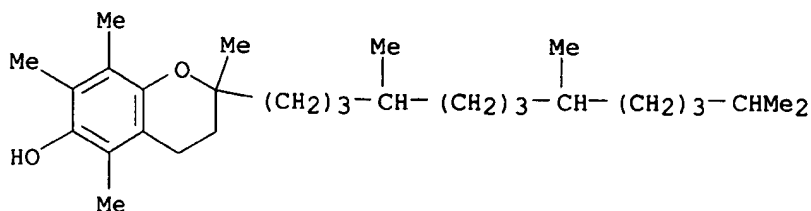
I

AB The synthesis of (all-rac)- α -tocopherol (I)

starting from trimethylhydroquinone and isophytol using fluorinated NH-acidic catalysts is described. The scope and limitations of this type of catalyst are discussed. The advantages of this new procedure are high yield and selectivity, no waste problem and mild reaction conditions. The best results in the synthesis of I (94% yield) using NH-acidic compds. are obtained in polar solvents. The used catalyst could be recovered.

REFERENCE COUNT: 25 THERE ARE 25 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L9 ANSWER 7 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2001:740313 CAPLUS
 DOCUMENT NUMBER: 136:71494
 TITLE: Industrial application of Nafion-systems in rearrangement-aromatisation, transesterification, alkylation, and ring-closure reactions
 AUTHOR(S): Schneider, M.; Zimmermann, K.; Aquino, F.; Bonrath, W.
 CORPORATE SOURCE: Vitamins and Fine Chemicals Division, Chemical Process Technology, F. Hoffmann-La Roche Ltd., Basel, CH-4070, Switz.
 SOURCE: Applied Catalysis, A: General (2001), 220(1-2), 51-58
 CODEN: ACAGE4; ISSN: 0926-860X
 PUBLISHER: Elsevier Science B.V.
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 IT 10191-41-0, Rac- α -tocopherol
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (Nafion-catalyzed cyclization reaction of trimethylhydroquinone with isophytol in preparation of)
 RN 10191-41-0 CAPLUS
 CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)- (9CI) (CA INDEX NAME)



AB Nafion, a perfluorinated sulfonic acid ion-exchange polymer, is known to be a very strong Bronsted acid. Thus, Nafion NR 50 and Nafion/SiO₂ with 15 weight % Nafion-loading were selected, in order to elucidate the potential for rearrangement-aromatization of ketoisophorone (KIP) to 2,3,5-trimethylhydroquinone diacetate (TMHQ-DA) in presence of acetic acid anhydride as acylating agent, transesterification of TMHQ-DA to 2,3,6-trimethylhydroquinone monoacetate (TMHQ-1-MA) and reaction of isophytol (IP) with trimethylhydroquinone (TMHQ) to (all-rac)- α -tocopherol. For the rearrangement-aromatization of KIP to TMHQ-DA supported Nafion/SiO₂ was markedly more active than the unsupported Nafion NR 50. Both Nafion-systems generally revealed remarkably high selectivity, which ranged up to 94 GC-a% TMHQ-DA at high conversion. The major side-product was 3,4,5-trimethylcatechol diacetate. In case of Nafion/SiO₂, pre-treatment under vacuum and especially grinding of the extrudates seemed to increase activity at comparably high

selectivity. Recycling Nafion/SiO₂ after filtering and rinsing with acetic acid anhydride led to gradually decreasing activity. Without intermediate isolation of TMHQ-DA, Nafion/SiO₂ was active and selective for the formation of TMHQ-1-MA. Using the Nafion systems in the reaction of IP and TMHQ revealed that remarkably high conversion of IP (>95%) and compared with zinc chloride/Bronsted acid or BF₃-catalyzed reaction good yields (≈92%) and selectivities were obtained. We found a strong dependency on the solvent polarity. In further expts., the recovery of the catalyst was tested.

REFERENCE COUNT: 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L9 ANSWER 8 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1995:818042 CAPLUS

DOCUMENT NUMBER: 123:314177

TITLE: Aluminum chloride-tetraalkylammonium halide complex as a novel catalyst ion Friedel-Crafts alkylation. Direct construction of the chroman structure from 1,3-diene

AUTHOR(S): Matsui, Makoto; Yamamoto, Hisashi

CORPORATE SOURCE: Sch. Eng., Nagoya Univ., Nagoya, 464-01, Japan

SOURCE: Bulletin of the Chemical Society of Japan (1995), 68(9), 2663-8

CODEN: BCSJA8; ISSN: 0009-2673

PUBLISHER: Nippon Kagakkai

DOCUMENT TYPE: Journal

LANGUAGE: English

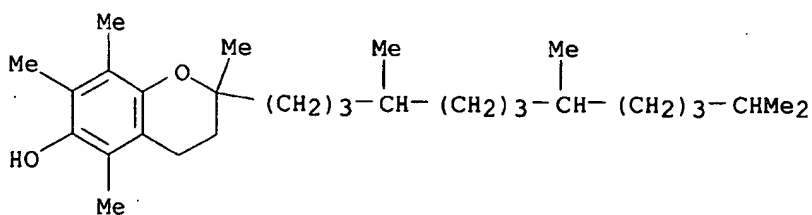
OTHER SOURCE(S): CASREACT 123:314177

IT 10191-41-0P, (±)-α-Tocopherol

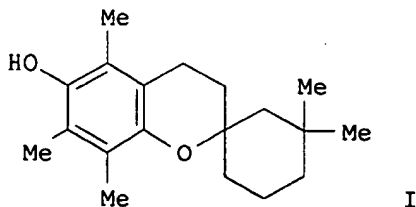
RL: SPN (Synthetic preparation); PREP (Preparation)
(aluminum chloride-tetraalkylammonium halide complex as a novel catalyst for Friedel-Crafts alkylation in construction of chroman structure from 1,3-diene)

RN 10191-41-0 CAPLUS

CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)- (9CI) (CA INDEX NAME)



GI



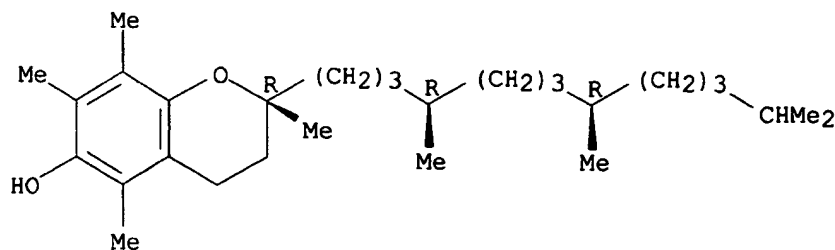
AB Tetrabutylammonium halides were found to accelerate Lewis acid-catalyzed Friedel-Crafts alkylation when trimethylhydroquinone and myrcene were used, followed by cyclization. to give the chroman compound I predominantly. For tetraalkylammonium salts which have long-chain alkyls and/or bromide, iodide counter anions promote the reaction in less-polar solvents. Phosphonium halides and sulfonium halide were also effective. The tetraoctylammonium bromide-aluminum chloride complex was an effective catalyst for the initial regioselective protonation of 7,11,15-trimethyl-3-methylene-1,6-hexadecadiene to give α -tocopherol in high yield.

L9 ANSWER 9 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1977:90092 CAPLUS
 DOCUMENT NUMBER: 86:90092
 TITLE: α - Tocopherols
 INVENTOR(S): Ichikawa, Yataro; Suzuki, Nobuo; Sawaki, Toru
 PATENT ASSIGNEE(S): Teijin, Ltd., Japan
 SOURCE: Jpn. Kokai Tokkyo Koho, 7 pp.
 CODEN: JKXXAF
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 51080859	A2	19760715	JP 1975-5290	19750111
PRIORITY APPLN. INFO.:			JP 1975-5290	A 19750111
IT 59-02-9P				
RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of)				
RN 59-02-9 CAPLUS				
CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-[(4R,8R)-4,8,12-trimethyltridecyl]-, (2R)- (9CI) (CA INDEX NAME)				

Absolute stereochemistry.



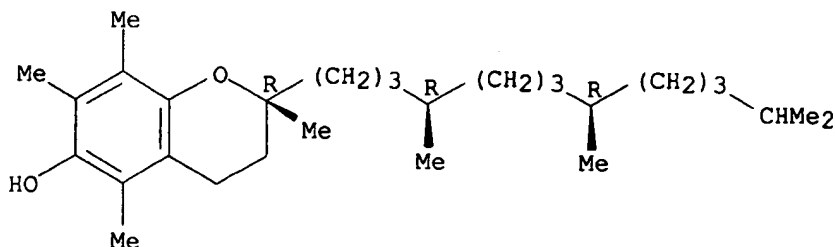
AB α - Tocopherols were prepared by reaction of phytol, isophytol (I), or their related compds. with trimethylhydroquinone (II) or its esters in the presence of Zn halides, which were isolated, treated with halogen donors, and recycled. Thus, 9.7 parts I in BuOAc was refluxed with a mixture of 5 parts II and 6 parts ZnCl₂ in BuOAc under N to give 92.1 mole% α - tocopherol (III) with 100% conversion of I. The aqueous layer from the H₂O-added reaction mixture was mixed with 0.5 part concentrated HCl, the mixture concentrated, and treated with AcOBu to remove H₂O azeotropically, and the AcOBu layer recycled to give 92 mole% III. HClO₄

and P tetrachloride were also used in place of HCl.

L9 ANSWER 10 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1976:74471 CAPLUS
 DOCUMENT NUMBER: 84:74471
 TITLE: Chroman ring-containing compounds
 INVENTOR(S): Ichikawa, Yataro; Yamanaka, Yoshiyuki; Yamamoto, Mamoru; Takeshita, Toru; Niki, Takao; Yamaji, Teizo
 PATENT ASSIGNEE(S): Teijin, Ltd., Japan
 SOURCE: Jpn. Kokai Tokkyo Koho, 21 pp.
 CODEN: JKXXAF
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 50089372	A2	19750717	JP 1973-140376	19731218
PRIORITY APPLN. INFO.: IT 59-02-9P			JP 1973-140376	A 19731218
RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of)				
RN 59-02-9 CAPLUS				
CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-[(4R,8R)-4,8,12-trimethyltridecyl]-, (2R)- (9CI) (CA INDEX NAME)				

Absolute stereochemistry.



GI For diagram(s), see printed CA Issue.
 AB Chroman ring-containing compds. were prepared by reaction of hydroquinones I (R1, R2 = H, C1-20 carboxylic acid group; R3, R4, R5 = H, Me) with R6CH2CH:CMech2R7 (R6 = OH, halo, C1-20 carboxylic acid group; R7 = H, C1-20 hydrocarbon group), R6CH2CH2CMech2R7, CH2:CHCMech2R7, or CH2:CHCMech2R7 in the presence of solid acids substantially not dissolving in the reaction system. Thus, a mixture of trimethylhydroquinone 1.326, phytol 2.582, SiO2-Al2O3 (87:13) 3, and perchloroethylene 30 parts was stirred 120 min under N to give 3.255 parts α -tocopherol. Also prepared were 2-(4-methylpent-3-enyl)-6-hydroxy-2,5,7,8-tetramethylchroman, 2-(4,8-dimethylnona-3,7-dienyl)-6-hydroxy-2,5,7,8-tetramethylchroman, 2,2,5,7,8-pentamethyl-6-hydroxychroman, tocopherol, α -tocopherol, and 5-methyltocopherol. Among other catalysts used in place of SiO2-Al2O3 were As2O3, TiO2, P2O5, ZnCl2, Fe2O3-Al2O3-SiO2, NiSO4-Al2O3, zeolite (H form), zeolite Na-Y, and bentonite.

=> log y
 COST IN U.S. DOLLARS

SINCE FILE TOTAL

10/494,005

FULL ESTIMATED COST	ENTRY 83.68	SESSION 250.83
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL
CA SUBSCRIBER PRICE	ENTRY -8.25	SESSION -8.25

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